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# A review of thermoelectrics research – Recent developments and potentials for sustainable and renewable energy applications

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ABSTRACT

In recent years, thermoelectric (TE) devices have emerged as promising alternative environmental friendly applications for heat pumps and power generators since the environmental issues such as the global warming and the limitations of energy resources gradually drew worldwide attentions. Due to the green feature and distinct advantages, the thermoelectric technology have been applied to different areas in an effort of designing simple, compact and environmental friendly systems. The applied areas are extended from the earliest application on kerosene lamp to aerospace applications, transportation tools, industrial utilities, medical services, electronic devices and temperature detecting and measuring facilities. The application potentials of TE in directly conversing thermal energy into electrical power have been identified, especially for where the cost of thermal energy input need not to be considered, such as waste heat utilization, in the light of the present low efficiency of thermoelectric conversion. The capability of TE in producing thermal energy (in terms of cooling or heating) with the use of electrical power is also well identified. This paper reviews the status of the material development and thermoelectric applications in different areas and discusses the difficulties in terms of the commercialisations of advanced materials. Other than this, the main purpose of this paper is to present the great potential of achieving both environmental and economic benefits by exclusively utilizing thermoelectric applications in different areas. It also comes to the conclusion that the thermoelectric applications with the current conversion efficiency are economically and technically practical for micro/small applications. However, it would be transformed to a more significant green energy solution for improving the current environment and energy issues by using medium/large scale thermoelectric applications when the thermoelectric materials with a figure-of-merit over 2 come into commercial practice.



**Contents**



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## 1. Introduction

Greenhouse gas has been increasingly emitted globally due to the increasing demand for electricity, heating, refrigerating, air-conditioning, etc. In the last few decades, immense efforts have been made to explore and develop alternative technologies to meet the increasing demand for energy. Green technologies, such as solar photovoltaic, wind turbine, hydrogenation and biomass, have started to play an important role in tackling the energy and environment issues arising in this technology oriented world. These technologies have brought us the undeniable benefits due to their clean style of power generation, which, to some extent, contributes to lessening the environment related issues. However, the greenhouse gas emission during the manufacturing process of these technologies cannot be ignored especially when a large amount of them is required. As we are all deeply aware inside, the overall energy demand of the world has never stopped climbing. The effort in developing the current green technologies and exploring new energy technologies only switches the pressure from traditional power technologies to different technologies. Something has not been changed, which is the increasing demands for energy. Turning our head back, we would be overwhelmed by the way how the resources are consumed. It is excessive and highly inefficient. This makes us wonder the essential cause of all related issues of global energy which have been seizing our attentions intensively. It is not the technologies themselves that give birth to the worries and anxiousness that the world is loaded with. Instead, it is ourselves, who have been consuming our finite resources in an excessive and wasteful style. We must appreciate the beauty of simplicity and reconsider the necessity of energy usage in many areas. Being equally important, the energy efficiency also needs to be enhanced by improving the system efficiency and recovering waste heat. In this paper, the thermoelectric (TE) technology, one of many green technologies, is reviewed to demonstrate its potential in improving the energy efficiency and point a possible direction of alleviating our energy demand.

## 2. Material development

Due to their low efficiency, the extensive applications of thermoelectric materials have been limited to specialised fields where the reliability rather than the cost is a major consideration. Considering the initial cost of establishing a thermoelectric system, thermoelectric applications with the current conversion efficiency are more suitable for small scale applications. The development of new thermoelectric materials with high efficiency is one of the key factors for expanding the range of thermoelectric applications to the medium/large scale. A “breakthrough” is needed for enhancing the figure-of-merit which is the thermoelectric characteristic that describes the thermoelectric performance of the materials. A great deal of efforts has been made in researching and developing materials with high efficiency and several typical methods have been used. These include super-lattice structure, plasma treatment, material segmentation and nanotechnology. Despite the success of achieving thermoelectric materials with high figure-of-merit, the commercialization difficulty is the barrier for most of the thermoelectric materials developed in research laboratories. This cause is attributed to the insufficient accuracy and difficult fabrication in material research and the practicality in material fabrication and device construction.

### 2.1. Function

Thermoelectric materials can be used for either cooling or power generation, as shown in Fig. 1. Its construction consists of arrays of N and P type semiconductors in which, by applying a heat source on one side and a cooler heat sink to the other side, electric power is produced and vice versa. Namely, electric power can be converted to cooling or heating by reversing the current direction.

Despite the low conversion efficiency of around 10% when used as power generators, they are strongly advantageous due to no moving parts. This made them both more reliable and durable compared to conventional energy technologies. Apart from that, they are scalable without releasing any pollutant to the environment during the operations. Hence, they would be ideal for applications in many areas at different scales replacing the traditional cooling and power generation methods.

In typical TE devices, the N and P materials are electrically connected in series and thermally connected in parallel in the form of flat arrays called modules. Fig. 2 shows a pair of thermocouple in a thermoelectric module working as a power generator. When there is a temperature gradient across the couple, the negatively charged electrons ($e^-$) in n-leg and the positively charged holes ($h^+$) in p-leg move from the heat source to the heat sink and conduct heat to the cold end. Consequently, a current flow is resulted from the initially uniform charge carrier distribution [1].

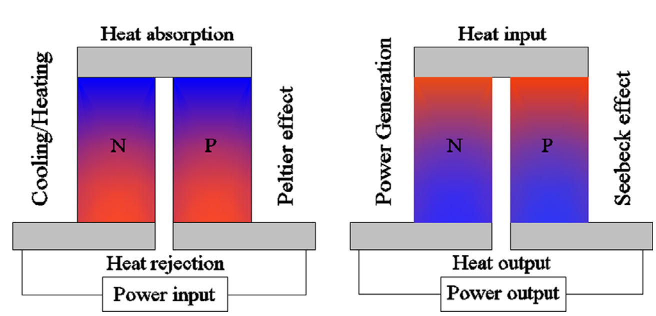



**Fig. 1.** Cooling/heating and power generation thermoelectric heat engines.

**Nomenclature**

| | |
|---|---|
| COP | coefficient of performance |
| $l$ | length of segment (mm) |
| $P_{input}$ | electrical power input (W) |
| $Q_c$ | cooling thermal power (W) |
| $S$ | Seebeck coefficient (V/K) |
| $T$ | absolute temperature (°C) |
| $T_c$ | cold side temperature (°C) |
| $T_h$ | heat source temperature (°C) |
| $\overline{T}$ | average operating temperature (°C) |
| $ZT$ | dimensionless figure of merit |
| $Z$ | figure of merit ($K^{-1}$) |

*Greek symbols*

| | |
|---|---|
| $\eta$ | conversion efficiency |
| $\beta_c$ | cooling effectiveness |
| $\lambda$ | thermal conductivity (W/m K) |
| $\rho$ | Electrical resistivity (Ω m) |
| $\sigma$ | electrical conductivity (S/m) |
| $\Delta T$ | temperature difference across thermoelectric module (K) |

Thermoelectric materials are evaluated by the figure-of-merit $ZT$, it is defined in terms of intrinsic material properties of both the N and P type materials and determined by three physical properties—Seebeck coefficient ($S$), electrical conductivity($\sigma$), and thermal conductivity ($\lambda$). It can be related to the physical properties by Eq. (1):

$$ZT=\frac{\sigma S^2}{\lambda}T; \tag{1}$$

where $T$ is the temperature. The figure-of-merit $ZT$ serves as a dimensionless parameter to evaluate the performance of a thermoelectric material. The larger the value of $ZT$, the better is the thermoelectric material. Obviously, the materials with higher electrical conductivity and lower thermal conductivity have larger value of $Z$ which contributes more to the enhancement of conversion efficiency $\eta$. It is given by Eq. (2)

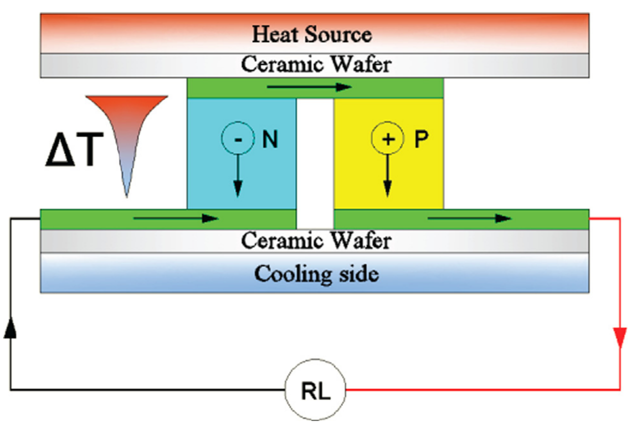



**Fig. 2.** Schematic diagram of thermoelectric generation.

$$\eta=\frac{\Delta T}{T_h}\left(\frac{\sqrt{Z\overline{T}+1}-1}{\sqrt{Z\overline{T}+1}+1-(\Delta T/T_h)}\right); \tag{2}$$

The conversion efficiency of electrical power to cooling is given in terms of COP (coefficient of performance), defined as

$$COP=Q_c/P_{input} \tag{3}$$

where $P_{input}$ is the electric power input and $Q_c$ is the cooling thermal power produced by TE module. The COP of TE module measures the cooling effectiveness of thermoelectric cooler. In an ideal assembly, the optimum cooling effectiveness can be expressed by

$$\beta_c=\frac{T_c}{\Delta T}\left(\frac{\sqrt{Z\overline{T}+1}-1-(\Delta T/T_c)}{\sqrt{Z\overline{T}+1}+1}\right) \tag{4}$$

where $T_c$, $\overline{T}$ and $\Delta T$ are the cold side temperature, average temperature of hot and cold sides, and the temperature difference.

### 2.2. Commercialization

The commercialization of thermoelectric materials involves the validation of a thermoelectric performance at the system level in commercial configuration. It is considered beyond the scope of the intended TE material research. The most famous commercialized thermoelectric material must go to $Bi_2Te_3$. It was recently reported that a material which is a promising candidate to fill the temperature

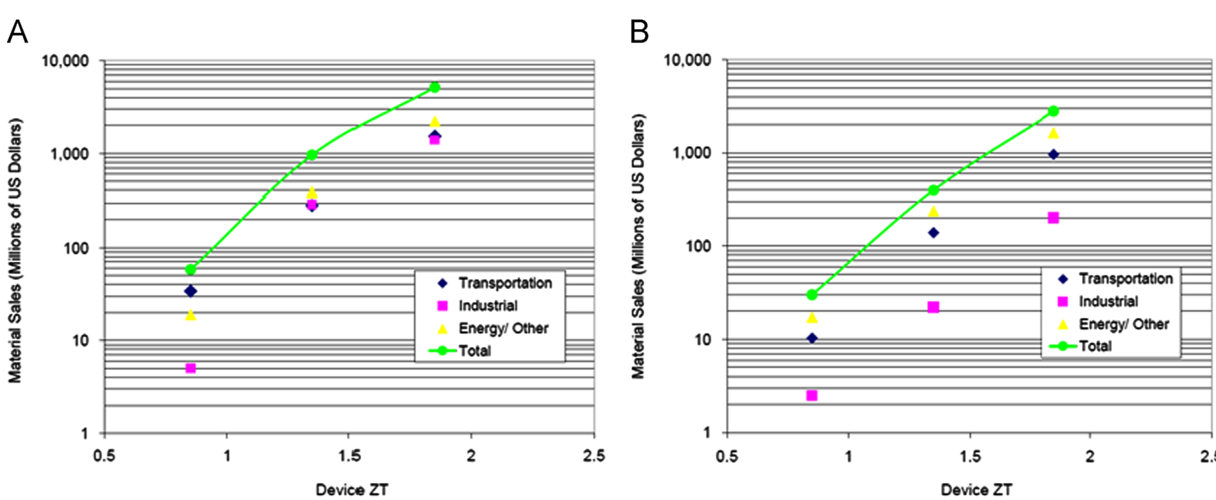



**Fig. 3.** TE Material Market, 2023 Projection (A) Power generation; (B) cooling/heating [3].

range in the *ZT* spectrum between those based on $Bi_2Te_3$ and PbTe is the semiconductor compound ß-$Zn_4Sb_3$. This material possesses an exceptionally low thermal conductivity and exhibits a maximum *ZT* of 1.3 at a temperature of 670 K. It is also relatively cheap and stable up to this temperature in a vacuum. Other new types of materials are coming up to market as exclusive researches are on-going to develop advanced modules. However, the commercialization of those materials is experiencing difficulties. They are included in material research, development and fabrication of TE couple and module and also design and construction of TE system.

Due to the limitation of testing equipment and measurement methods, some of the materials with the claimed high *ZT* are not reproducible and the relevant experiments are unrepeatable. The properties change with time and exposure to test conditions which leads to insufficient accuracy. For fabrication of TE element and modules, the fabrication of TE couple requires time consuming procedures for fabricating the N and P type elements with the expected level of electrical and thermal resistance. The wrong fabrication would lead to the degradation of couple performance. However, the successful fabrication of TE couple has been proven to be difficult using the experimental materials produced in research laboratories. Furthermore, the fabrication of low thermal and electrical interface resistivity makes the metalizing process difficult since the current metallization procedures are immature. The measurements of interfacial resistances are also difficult and time consuming. For the fabrication of TE module, reliable, repeatable, economical and durable fabrication methods are needed for connecting large arrays of TE couples with the capability of accommodating thermal expansion, mechanical shock as well as other physical conditions and withstanding the necessary environmental conditions.

For the design and construction of TE system, design methods and construction tools for developing stable, durable and environmentally compatible TE system need to be standardized. The cost, performance, usage and final disposal of the system need to warrant commercial development [2]. Although TE materials have various applications in many areas, there is still a long way to go to the commercialization. Most published announcements of improved TE materials note the commercial need of better materials, with the implication that the materials described will enable, or at least constitute a significant step towards, meeting market needs. Fig. 3(A) presents projections for sales of power generation materials as a function of *ZT*, assuming materials are available with an average *ZT* of 2 by 2018 and are mass produced by 2023. Fig. 3(B) presents market projections for cooling/heating materials under the same assumptions. The results show that market size is a strong function of *ZT*, for device level values up to about 2.

However, there has been no breakthrough in developing new commercial material with superior *ZT* which can displace $Bi_2Te_3$ or the other materials previously at the device level in the last two decades. Several causes can be identified as follows [4]:

Some of the claimed higher values of *ZT* have not been reproducible because of measurement errors in one or more of the intrinsic properties that constitute *ZT* (i.e., $\alpha$, $\lambda$, $\rho$).

1. Usually, materials are fabricated in a form factor suitable for testing by a particular, specialized type of equipment.
2. Samples fabricated as thin films (1–10 μm thick) tested in plane may have surface dislocations, substrate interactions, or stress-induced effects that skew results. Quantitative corrections for these effects are difficult and time consuming.
3. Inadequate test equipment or simple test errors, has (infrequently) resulted publication of erroneous or non-repeatable measurements.
4. Individual properties, if measured sequentially, can change with time or exposure to test conditions. The resulting computed *ZT* can be misleading.
5. In some cases, two material properties (e.g. $\alpha$ and $\rho$ in thin films) have been measured and the third property (e.g. $\lambda$) extrapolated or inferred (erroneously) from the literature and used to compute artificially high values of *ZT*.

Commercialization is a key factor for thermoelectric research and development. In all of the Science and Nature magazine articles published since 2000, which have discussed development in TE, the authors referenced the commercial need for better TE materials in their introductions [5]. However, the commercialization process is going to take a long time.

TE systems appear to be as green as another emerging solid state energy conversion technology, photovoltaic (PV). The comparison discloses that the research in each has been extending over about the same period of time, and in each case, the commercialization has been impeded by similar barriers of high cost per watt output and low efficiency. Progress over the past two decades suggests that new TE material technology will be too slow to make significant commercial impact unless new approaches are taken to accelerate material development.

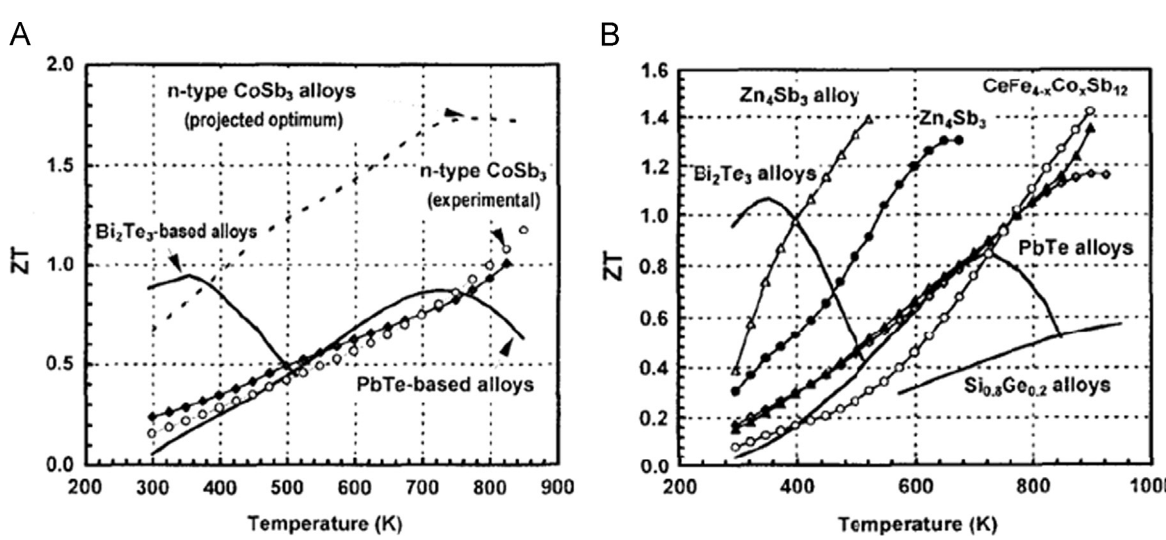



**Fig. 4.** *ZT* values of state of the art and JPL improved thermoelectric materials as a function of temperature (A) N-type; (B) P-type [39].

### 2.3. Development of high efficiency thermoelectric modules

Since the discovery of the Seebeck effect, thermoelectric modules have been studied for more than 180 years. Nevertheless, the thermoelectric module has not become widespread yet. The major reason for this is the low conversion efficiencies of conventional thermoelectric modules. The development of more efficient materials and devices is the key to expanding the range of application of thermoelectric applications and it involves improving the three physical properties: Seebeck effect, thermal conductivity and electrical resistivity.

A broad research and development for advanced thermoelectric has been conducted by JPL which has identified and retained several categories of materials by using several physical and chemical criteria. Among discovered materials, the skutterudite and $Zn_4Sb_3$-based materials are particularly promising and were developed and optimized by Fleurial et al. [41]. The materials with figure-of-merit over 1 cover a wide range of temperatures: p-type $Zn_4Sb_3$-based materials (375–675 K), p-type Ce-based filled skutterudite (675–975 K), and n-type heavily doped $CoSb_3$ (525–975 K), shown in Fig. 4.

It was shown that further improvements in the thermoelectric performance are possible. Since then, an increasing effort in discovering and developing materials with figure-of-merit higher than 2.0 has been stimulated [6]. The following methods are introduced with regard to improving $Z$ value. They include super-lattice, plasma treatment, segmented element nano-composite and nanostructure.

#### 2.3.1. Super-lattice

Due to the classical and quantum size effects on energy carriers, energy transport in nanostructures differs significantly from that in macrostructures. It was proved that [7] the thermal conductivity values of nanostructures such as super-lattices are lower than that of their bulk constituent materials. This reduction leads to a large increase in thermoelectric figure-of-merit in several super-lattice systems, which are anisotropic. It improves $ZT$ along both the parallel (in-plane) and perpendicular (cross-plane) direction to the film plane by the enhancement of the electron performance through taking advantage of sharp features in the electron density of state and reduction of phonon thermal conductivity through interface scattering [8]. The other involved mechanisms for the improvement of electron performance include electron energy filtering [9] and thermionic emission [10]. Experimental studies have demonstrated that a significant thermal conductivity reduction in a wide variety of super-lattices can be achieved [11].

The idea of using super-lattices to improve the figure-of-merit through the reduction of phonon thermal conductivity and enhancement of electronic conductivity was first discussed by Dresselhaus, Harman, and Venkatasubramanian [12]. In their publications, the quantum size effects on electrons drew wide attention and inspired intense theoretical and experimental researches on the thermoelectric properties of quantum wells and super-lattices [13]. It has been applied on several materials ($Bi_2Te_3/Sb_3Te_3$ [14]), among which $Bi_2Te_3$ super-lattices and PbTe-based quantum dot super-lattices showed the most impressive results [15, 16], shown in Fig. 5.

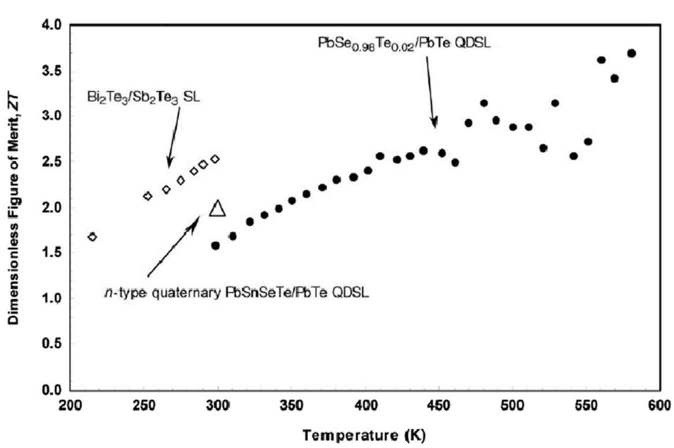



**Fig. 5.** Thermoelectric figure of merit $ZT$ for $Bi_2Te_3/Sb_3Te_3$ super-lattices, PbTe-based quantum dot super-lattice [17].

A comprehensive summary of researches in super-lattices has been done by Boettner et al. [18]. However, super-lattices grown by thin film deposition are limited to niche applications.

#### 2.3.2. Plasma treatment

Different methods have been adopted to improve the performance of thermoelectric element by Seijiro [19]. For BiTe-based materials, two methods, which have been used, include surface treatment and shifting $Z$ value.

Plasma treatment using various types of coating was applied to treat the raw material powder as it was predicted that reducing powder by hydrogen would improve the powder characteristics because of low oxygen concentration. Fig. 6 shows examples of the results of powder treatment by hydrogen plasma and oxygen plasma, respectively. The removal of many micro-deposits from the powder surface can be seen (Fig. 7). It proves that a lower oxygen concentration obtains a low oxidation of the powder surface and the figure-of-merit is improved as the oxygen concentration decreases, which is shown in Fig. 8. It makes it clear that isolating the plasma treatment process from oxygen is necessary.

Fig. 8 shows the relationship between oxygen concentration and figure of merit, obtained with a p-type, Bi-Te-based thermoelectric material. It can be seen that the figure-of-merit improves as the oxygen concentration decreases.

Shifting peak value of figure-of-merit was proposed in reference [19] to improve the performance of BiTe-based thermoelectric elements. By adjusting the carrier concentration to improve the high temperature characteristic and changing the composition to

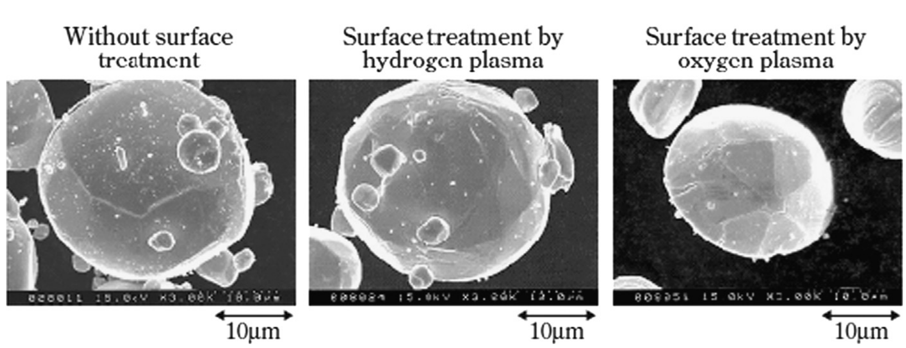



**Fig. 6.** Examples of results of surface treatment by plasma [19].

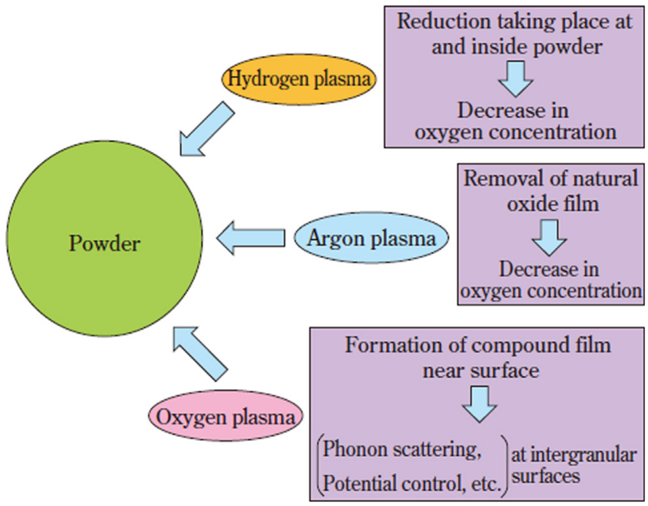



**Fig. 7.** Concept of surface treatment of powder [19].

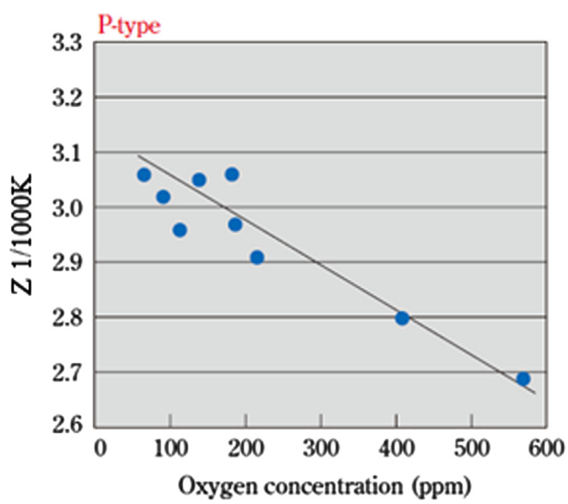



**Fig. 8.** Relationship between oxygen concentration and performance index [19].

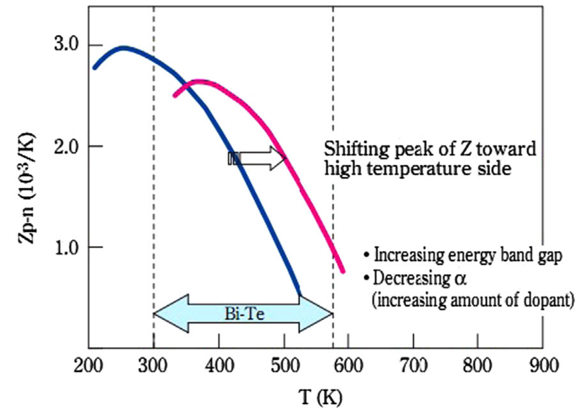



**Fig. 9.** Shifting *Z* value.

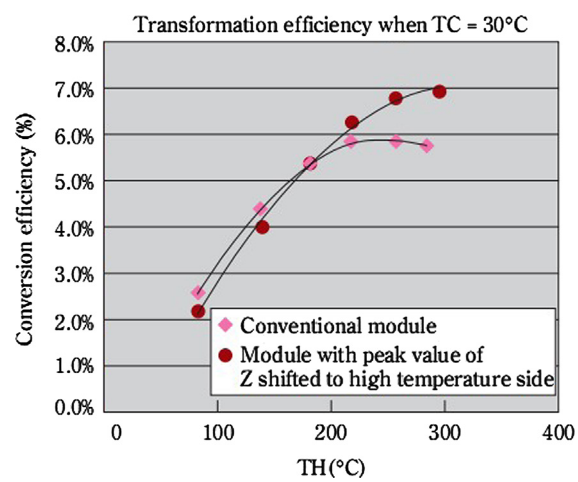



**Fig. 10.** Conversion efficiency when *Z* shifts to high temperature side.

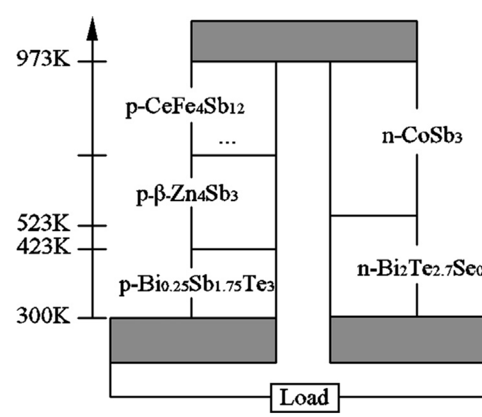



**Fig. 11.** Schematic of a segmented thermoelectric generator using segmented thermoelectric material developed at JPL [20].

control the energy band gap, the peak *Z* could be shifted to high temperature side, the result is shown in Fig. 9. They obtain a thermoelectric conversion system efficiency of 6% in view of the thermoelectric conversion efficiency of conventional waste incinerators is 3.6% (Figs. 10, 11).

N-type Bi-Te-based maintains an improved characteristics (large *Z*) in high-temperature region without a significant decrease in that of the low-temperature, whereas *Z* reduces remarkably in low-temperature region if it is p-type. Nonetheless, the average performance index is improved across the entire working temperature range.

### 2.3.3. Segmented material

No single thermoelectric material is suitable for operating over a very wide range of temperature. It brings about the problem of converting heat over a large temperature difference range. From material wise, segmented material can solve this problem by using different materials in each temperature range where they possess optimum performance. The segmented materials have p-type and n-type legs formed of different segments joined in series. The first generation was developed in JPL (Jet Propulsion Laboratory) and the concept is shown in Fig. 12 [20]. Compared to those using the state-of-the-art single material, the benefits of using these segmented materials include operation over a large temperature difference range and large average value of figure of merit.

The optimum design of the geometry of segmented materials involves primarily fine tuning the cross section and length of the different segments. With the given average thermoelectric properties (Seebeck coefficient, electrical resistivity and thermal conductivity) over the temperature range that each segment operates at, the optimum cross section, length and optimum current

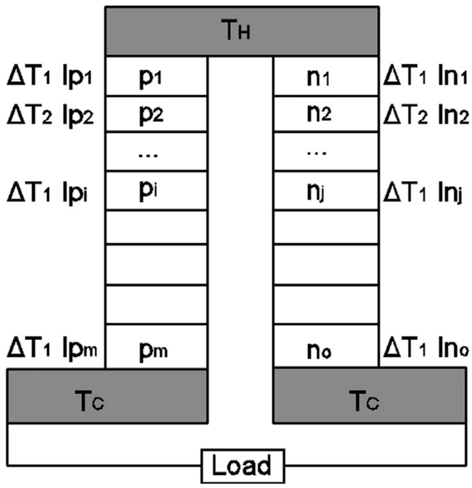



**Fig. 12.** Schematic of segmented material [20].

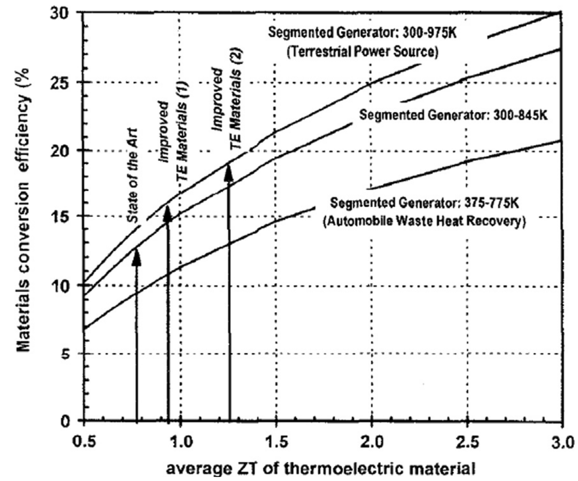



**Fig. 13.** Calculated thermoelectric materials conversion efficiency as a function of *ZT* for various segmented generators operating at different delta *T* [22].

and efficiency can be calculated [21] using Eqs. (5)–(7):

$$\frac{\lambda_{p_i}\Delta T_{p_i}}{l_{p_i}}=\frac{\lambda_{p_{i+1}}\Delta T_{p_{i+1}}}{l_{p_{i+1}}} \tag{5}$$

$$\frac{\lambda_{n_i}\Delta T_{n_i}}{l_{n_i}}=\frac{\lambda_{n_{i+1}}\Delta T_{n_{i+1}}}{l_{n_{i+1}}} \tag{6}$$

$$L=\sum_{i=1}^{m} l_{p_i}=\sum_{j=1}^{o} l_{n_j} \tag{7}$$

where $\lambda$, $l$ and $\Delta T$ are the thermal conductivity, the length of each segment and temperature difference across each segment, respectively. $L$ is the total length of the legs.

In the direction of current flow, different thermoelectric material forms segmented elements and each operates its superior performance over its temperature range. Materials of good electric conductors and poor thermal conductors are intended to be discovered to expedite the development of high-efficiency.

Based on the results achieved to date at the Jet Propulsion Laboratory (JPL) on novel materials, the performance of an advanced segmented generator design operating in a large temperature gradient (300–945 K) is predicted to achieve about 15% conversion efficiency. This would be a very substantial improvement over state-of-the-art thermoelectric power converters. Such a terrestrial power generator could be using waste heat or liquid fuels as a heat source [22]. Fig. 13 shows the conversion efficiency as a function of *ZT* for a thermoelectric generator operating between different temperature differences with the advantages of using materials with better thermoelectric performance and of operating at larger $\Delta T$.

### 2.3.4. Nano-composite

Nano-composite structure thermoelectric material is the thermoelectric material mixed with impurity, such as nanoparticles (insulating, semiconductor or metal) or nanometre-sized hollow [23]. It was said to represent one promising approach that fabricates thermoelectric materials with high figure-of-merit. It is generally believed that the strong phonon scattering effect in the transmission caused by incorporation of nanoparticles is the main reason of improving the thermoelectric properties of nano-composite thermoelectric materials.

The idea of nano-composites was inspired by the conclusion that the reduced thermal conductivity in super-lattices comes from the sequential interface scattering of phonons rather than the coherent superposition of phonon waves. Hence, the nano-composites can be a cheaper alternative of super-lattices to obtain materials with high figure-of-merit [24], [25]. The challenge is choosing the mismatch in electronic properties properly between the constituent materials thus the electron transport properties can be maintained or even enhanced.

In the semiconductor, electricity is carried by the electrons and holes, and energy is transmitted by lattice vibrations and phonon. However, currently there are little theoretical or modeling works that have been done in the literature related to thermoelectric properties of nano-composites that one can rely on to achieve good design of nano-composites. The reason lies in the fact that there are a variety of challenges in simulation of both electron and phonon thermoelectric transport in nano-composites and the inspection of the wave effect in transport processes in nano-structure [26]. Worlock [27] first studied the phonon scattering after mixing nano-particles. Vining [28] presented his theoretical calculations which lead to a result that mixing free dispersed nano-particles can reduce the thermal conductivity without affecting its electrical transmission performance.

In the advances of nano-technology leading to high efficiency, complex bulk materials including skutterudites, clathrates, and Zintl phases have been explored. By decoupling the conflicting properties, these complex high efficiency materials give way to further enhancement in cell arrangement such as diversifying array of complexity within the unit cell, of nano-structured bulk, or of thin-film multi-layer structures.

Kanatzidis [29] demonstrated a new method: the incorporation of nano-particles in situ precipitation method. This method is adding certain percentage of antimony, lead, silver and tellurium into melting pot, which melts at about 800 °C for 4 h, then the temperature, is maintained at 400 °C for 40 h and finally cooled down to room temperature. This method shows the advantage of simple and inexpensive process as well as being effective in avoiding agglomeration of nanoparticles.

### 2.3.5. Nano-wires and nano-tubes

Quantum wire can improve the density of states more than quantum well, theoretical calculations of the lower dimensional structure show that nano-wires may have a better thermoelectric properties than the super-lattice [30]. It is theoretically expected that the diameter of quantum wire will be less than 10 A and the *ZT* value of material will be more than 10.

Current preparation methods for one-dimensional nano-wire are mainly gas condensation method [31], electrochemical method [32–35] and high-pressure injection method [36–38]. Zeolites, alumina template and the porous polymers are good template

materials for nano-wire growth. Bi [38], $CoSb_3$ [32], $Bi_2Te_3$ or $Bi_{1-x}Sb_x$ [34] nano-wires can be obtained by the above methods and their Seebeck coefficients are superior to conventional materials. In addition to the previously mentioned ways, there are also examples which use silicon mold technology. Using micro-machined silicon wafer as the mold, micro thermoelectric devices are prepared and there are 10,000 pairs of $Bi_2Sb_2Te$ columnar array PN junction (depth about 300 μm, side length about 40 μm) arranged in one square centimeter on them. Silicon mold technology can take advantage of the mature silicon wafer micro-machining technology to produce complex shapes, ultra-fine silicon mold, combine micro-fabrication technology in micro-electromechanical systems (MEMS) and material forming technology together. Although the obtained nano-wires have not yet been small enough in size, silicon mold technology has played a very good reference for future applications in micro-device.

Zhao′s research team [39] used hydrothermal synthesis to obtain $Bi_2Te_3$ compounds nano-tubes and nano-capsules (diameter 100 nm), then added them to the n-type $Bi_2Te_3$ thermoelectric material to form nano-composites. Comparing to traditional zone-melting method, the material′s conductivity has been improved significantly, the thermal conductivity decreases significantly(only 0.3 W/(m K) at 473 K), the *ZT* value reaches 1.0 or more, even more than the highest value of commercialized thermoelectric devices presented by Tritt et al. [40].

The study of quantum line transmission performance shows that its diameter′s being equal to or less than 2 nm is necessary [41]. The measurements of nano-wire conductivity and thermal conductivity make it difficult to study nano-wire thermoelectric materials.

### 2.3.6. Structure/geometry

In addition to the conventional method of modifying the competitiveness of thermoelectric materials by improving the figure-of-merit, another direction is developing the novel thermoelectric module shapes. Thermoelectric modules have typically plate-like shapes and are fabricated from bulk semiconductors such as $Bi_2Te_3$ and PbTe, making them rigid and unfit for non-flat surfaces (e.g. circular tubes) used in waste heat recovery applications where the heat flow is perpendicular to the ceramic plates. When heat flows in radial directions, the attachment of flat modules around a cylindrical heat source is often complicated. Hence, it is highly necessary to fabricate thermoelectric modules which can conform easily to the curved surface. Thin film thermoelectric module is an invention that overcomes this technical issue, one example is shown in Fig. 14. It is a type of thermoelectric power generator that is based on thin film with flexible fiber substrates. A thin film module produced by screen printing is mentioned in [42]. Another novel tube-shape thermoelectric module for power generation has also been developed recently by Min and Rowe [43]. It is fabricated from four ring-shaped thermo-elements and its performance in electrical power generation is evaluated by measuring the power output as a function of temperature difference across the device. It was concluded that a tube-shape thermoelectric module could achieve similar performance to that of a conventional flat module, and has an advantage in waste heat recovery applications where heat flows in a radial direction. As 3D printing technology becomes more and more popular, flexible and bendable thin film thermoelectric produced by 3D printing is gradually floating onto the surface. This printable thin film thermoelectric module would tremendously enhance the applicability of thermoelectric devices.

## 2.4. Summary

Table 1 summarizes the researches that develop advanced thermoelectric material using different materials and approaches.

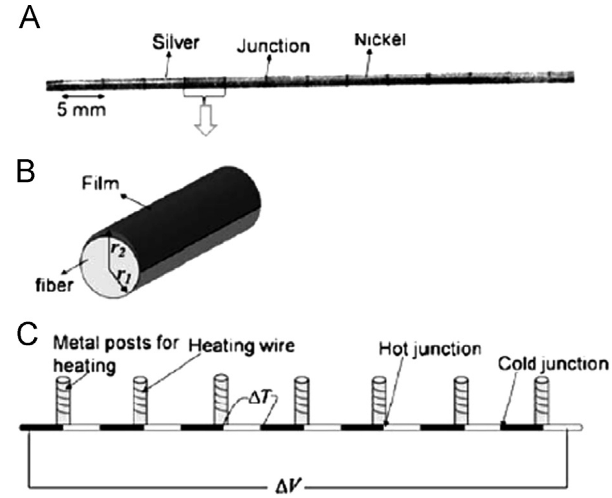



**Fig. 14.** Schematic diagram of thin film thermoelectric module (a) striped thin film thermoelectric fiber made with thermal evaporation of nickel and silver; (b) fiber with thin film deposited on one side; (c) experimental setup for applying a temperature difference and measuring the induced open circuit voltage [44].

The references cited in the table are mainly experimental studies which present the result from different perspectives. Materials, non-dimensional figure of merit (*ZT*), operating temperature and conversion efficiency are used to present the major results. The commercialization difficulty is the barrier for most of the thermoelectric materials developed in research laboratories. This cause is attributed to the insufficient accuracy and difficult fabrication in material research and the practicality in material fabrication and device construction. However, the methods listed in Table 1 have shown positive results by changing the material properties and improving module shape and structure, such as reducing thermal conductivity, enhancing electrical conductivity and adopting novel module shape and structure, such as ring-shape and thin film. More efforts are being made to develop and commercialize the advanced materials with higher figure of merit which could make the applications economically feasible.

## 3. Application

Due to the distinct advantages, thermoelectric devices have been utilized or attempted to be used in areas like aerospace applications, transportation tools, industrial utilities, medical services, electronic devices and temperature detecting and measuring facilities.

Compared to PV which is also solid-state green technology, thermoelectric power generation gives lower energy conversion efficiency. However, due to the great potential of power generation by using solar radiation and any other kinds of possible heat sources as well as the reliable long period maintenance-free operation, thermoelectric generators have become technically attractive. It is very suitable for power generation by using solar radiation and recovering heat from waste heat sources due to the low cost or free use. Relevant investigations have been carried out to seek for optimum and sustainable ways of using them to the maximum level.

### 3.1. Heat engine applications

A conventional cooling system contains four fundamental parts which are evaporator, compressor, expansion valve and condenser. The evaporator or cold section is the part where the pressurized refrigerant expands, and evaporates. Energy is absorbed during this state change. The compressor acts as the refrigerant pump.

**Table 1**
Development methods for advanced thermoelectric materials.

| Application | Area | References | Material | Purpose (s) | Operating temperature (cold/hot) | Power input (output) | Conversion efficiency | Thermal efficiency | Institute (s) |
|---|---|---|---|---|---|---|---|---|---|
| Heat engine | Vehicle | [45] | BiTe based | Cooling and heating | Not specified | n/a | n/a | Not specified | Amerigon Inc. |
| | Medical service | [46] | Not specified | Cooling | 283 K/318 K | 12 V/4 A | n/a | Not specified | Gazi uni |
| | Electronic | [47–51] | CdZnTe | Cooling | 283 K/313 K | 3 W | n/a | Not specified | Leicester uni, Amptek Inc. etc. |
| Power generations | Automobile | [61,62] | $Bi_2Te_3$, PbTe | Electricity generation | 373 K/1073 K | 0.5–1 kW | 5–10% | n/a | Science uni of Tokyo |
| | Aerospace | [73] | PbTe, SiGe | Electricity generation | 366 K/ 783 K – 1300 K | 25–56 W | Not specified | n/a | Cardiff uni |
| | Industrial | [80–82] | SiGe | Electricity generation | 293 K/871 K | 46.8 W | 4.4% | n/a | Shonan Inst. of Technol |
| | Domestic | [84,87–89] | $Bi_2Te_3$, PbTe | Electricity and hot water generation | 303 K/ 473 K – 911 K | 4 W–1 kW | 4.0% | 60%–80% | Nottingham uni, Cardiff uni, etc. |
| | Thin film | [92] | ZnSb, $Bi_2Te_3$ | Electricity generation | Not specified ($\Delta T$=85 K) | 19.13 μW | Not specified | n/a | Shenzhen uni |

*Note*: the one that is not given in the references is “Not specified”; “n/a” stands for not applicable.

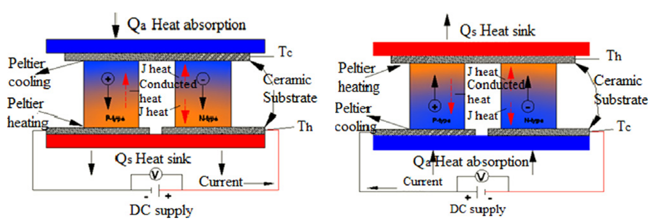



**Fig. 15.** Schematic diagram of Peltier effect for cooling and heating.

The condenser dissipates the heat absorbed at the evaporator plus the heat produced during compression, into the environment. For thermoelectric coolers based on the same fundamental laws of thermodynamics with the conventional heat pumps, they are solid-state heat pumps without moving parts, without using fluids or gases. They have compact and simple structure with quiet and maintenance-free operation. For heating and cooling applications, the TE energy conversion is called “Peltier effect” (also called TEC), where a temperature difference is created across two dissimilar legs of semiconductor material by supplying an electric current through the legs, which are shown in Fig. 15. At the cold junction, heat is absorbed by electrons as they pass from a low energy level in the p-type semiconductor element, to a higher energy level in the n-type semiconductor element. The power supply provides the energy to move the electrons through the system. At the hot junction, energy is expelled to a heat sink as electrons moving from a high energy level element (n-type) to a lower energy level element (p-type).

### 3.1.1. *Vehicular heating and cooling*

Solid state heating/cooling technologies in vehicles with few moving parts if any are much favoured by vehicle architectures. Conventional vehicular HVAC systems include mechanical refrigerator and absorption refrigerators. Conventional vehicular HVAC, which has notably high coefficients of performance and good reliability in spite of the moving parts, involves with complex system structure, noisy operation, usage of refrigerant and large vehicle space. Meanwhile, the latter one, which can operate with less noise using almost any kind of heat sources, has a relatively low coefficient of performance due to the combination of heat pump and heat engine. Another problem is that it only works properly when installed without being tilted.

It has to be admitted that thermoelectric refrigerators are much less efficient than mechanical refrigerators when operated in the suited conditions. However, unlike mechanical refrigerators, thermoelectric coolers can maintain the efficiency down to very low cooling power, even at the order of milliwatts. In addition, they operate silently without any moving parts, with no working fluids to leak away. This fact gives these devices an extremely long working life especially when the care is taken in the process of design and construction. The real benefit that comes from the flexibility is its operation in conjunction with a proportional control way rather than the on–off style. Therefore, thermoelectric device is a candidate solution for vehicular HVAC.

They have been used to cool or heat car seats by several major car manufacturers including Ford, GM, Hyundai, Jaguar, Nissan, Range Rover and Toyota [45]. The boarder use has been enabled by the improved thermodynamic cycles and advancements in device architecture which enhances the cooling and heating efficiency and reduces the amount of used material, respectively. The current climate control system for vehicular heating and cooling, which has been widely used, is presented by Amerigon and shown in Fig. 16 and Fig. 17.

Due to the role in improving the fuel economy of TE, the trend that it has been transforming from assistant HVAC device to the main role in vehicle cooling and heating system is becoming increasingly obvious. One advantage of TE HVAC system is that the cooling and heating can both be achieved and switched by just simply reversing the current. When operating in heating mode, TE devices can readily have COPs at 2–3 without going through energy-consuming procedures, whilst the traditional HVAC system needs to pump the extracted thermal energy into working fluids to deliver to other components where another heat exchange procedure occurs to finish the transfer with lower COP.

Compared with current systems, cooling/heating using currently available thermoelectric materials could provide significant advantages such as improved fuel economy, reduced toxic and greenhouse gas emissions. TE HVAC systems could be designed to take best advantages of thermoelectric. Compact thermoelectric units can be installed in the seats, dashboard and overhead for the driver and the front seat occupant. Units can be installed in the

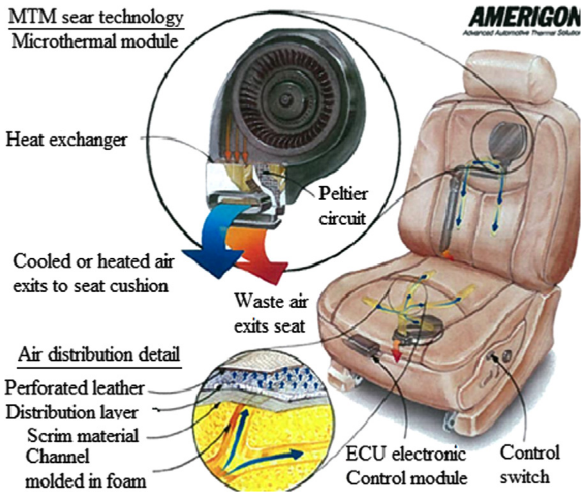



**Fig. 16.** Vehicular Climate Control System amounted in seat [45].

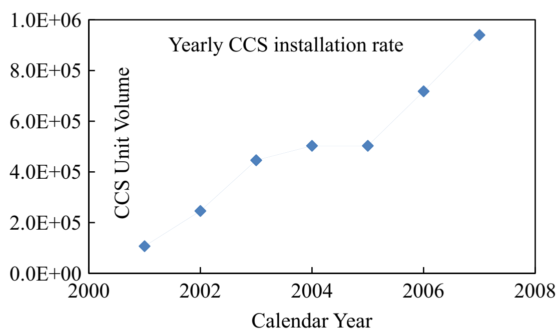



**Fig. 17.** Yearly installation rate of CCS between 2001 and 2007.

back of the front seats, the overhead, seats and floor. These units can be devised to only cool or heat the person, not the whole cabin. The driver can be cooled with less than 700 W of cooling whereas current air conditioners need to provide up to 3500–4000 W. It can be also remotely activated 50 m or so from the vehicle.

As the TEGs and TE HVAC systems are introduced in vehicles, the volume should result in lower cost and greater availability of thermoelectric for an extended range of applications. This should also significantly enhance the support for development of more efficient thermoelectric devices and commercially viable fabrication.

#### 3.1.2. Medical service and food industry

In medical area, it is important to keep vaccination, blood serum and other biological products within certain temperature range for storage and transportation purpose. The properties will stabilize in the range of medical requirements. A portable thermoelectric medical cooling kit controlled by a microprocessor was developed for preserving human blood during transportation. It operates with 12 V dc and 4 A [46]. In remote regions of developing countries like India and China, this new method shows a trend of more flexible ways of transporting medical products and travel doctors. Also, it could make on-door medical visits and dealing urgent medical issues possible. This thermal requirements also apply to the food industry which needs certain temperature control during the process of food transportation and storage.

#### 3.1.3. Electronic device

In electronic engineering areas, many electronic devices with high power, such as power amplifiers and microprocessors, operate at high temperatures close to the edge of reliability. This could cause severe impact on the performance and lifetime. Thus, cooling is needed to improve the performance and lifespan of the devices. The conventional devices are not well suited in these applications due to the need of large cooling area. For the power device with high density structure, the difficulty becomes more obvious for the conventional cooling techniques due to the large heat fluxes. The thermoelectric coolers can deal with this problem by effective local cooling. They can also operate quietly due to no moving parts. For example in Fig. 18, an application has been used to improve the accuracy of electronic instruments by reducing the thermal noise of the electric components and the leakage current of the electronic devices [47–49]. One of the examples is a cooled CdZnTe detector for X-ray astronomy. Cooling between 30 °C and 40 °C reduces the leakage current of detector and allows the use of a pulsed reset preamplifier and long pulse shaping times, significantly improving the energy resolution. Although the heat is conducted from the very low temperature 40 °C to the chilled water of 10 °C, it is only necessary to use 3 W of electrical power for this small capacity application.

In the aforementioned applications, an electronic device to be cooled is usually mounted directly on the cold side of one or more thermoelectric devices allowing maximum thermal transfer between the electronic device and the cold side. The hot side of the thermoelectric device is coupled to a heat sink and a fan or water is used to cool the hot heat sink in recent applications. Nature convection is also used in some cases. A variable source of direct current connected to the thermoelectric coolers to allow them to lower the temperature of the electronic devices.

Thermoelectric cooling can also be used to work with solar PV for electrical power generation. Better performance and cheaper cost were obtained when thermoelectric modules are used to actively cool solar PV than when used to recover heat from solar PV panel [51]. Attempts have also been made to employ thermoelectric Peltier modules in windows to supply warm air to residential space. However, the heat output was not enough to supply sufficient heat to the living space.

### 3.2. Thermoelectric generator applications

Its application can be classified into two main categories according to the application style, host application and parasitic application. In host application, all heat in the heat source is for the energy conversion whilst in parasitic application, the heat is partially converted to electricity without affecting the main functions. Available heat sources with a wide range of temperatures exist for these applications, from low grade waste heat, at 325–350 K, to high grade waste heat 850–1100 K.

#### 3.2.1. Automobile

The attraction of the application in automobile lies in the reduction of fuel consumption, and thus environmental impact. The first trial happened in 1914 when thermoelectric generator was used to recover some of waste heat energy from reciprocating engines and this technology was patented, which is shown in Fig. 19. The heat was provided by the exhaust gases in the pipe while the heat sink is functioned by circulated cooling water.

A more recent application example is given by a patent shown in Fig. 20. In this application, a pump is used to supply cooling water through each cooling water circulation paths. The cooling water circulation path includes a cooling water pipe arranged along the exhaust pipe to pass the cooling water.

Fig. 19 shows no cooling method for this application, although cooling water was suggested. In Fig. 20, the cooling water is circulated by cooling water pump to cool down the cold side of

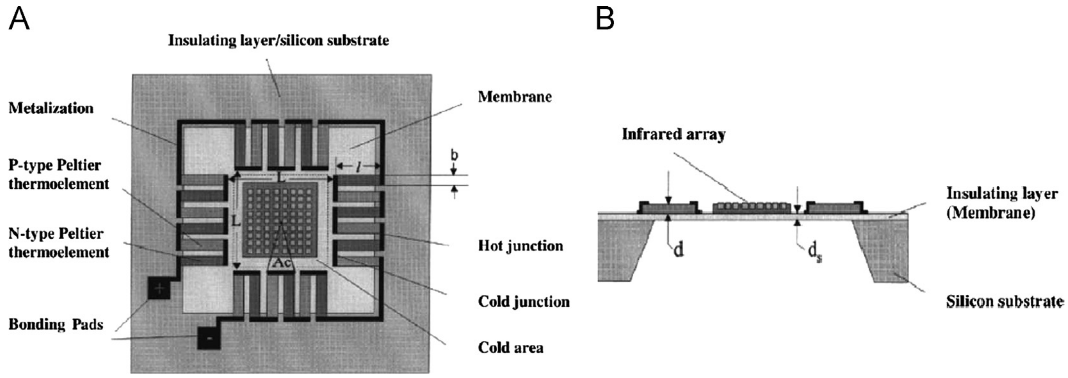



**Fig. 18.** Schematic diagrams of an integrated thermoelectric micro-cooler with infrared components integrated onto cooled central region (a) Plane view and (b) cross-sectional view [50].

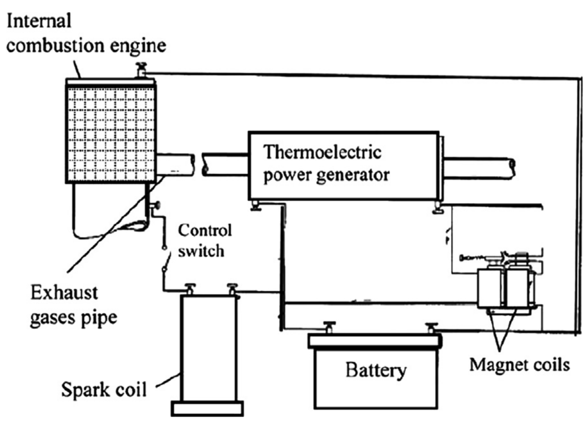



**Fig. 19.** Schematic diagram showing early invention of converting waste heat into electrical power applied to an internal combustion engine using a thermoelectric power generator [52].

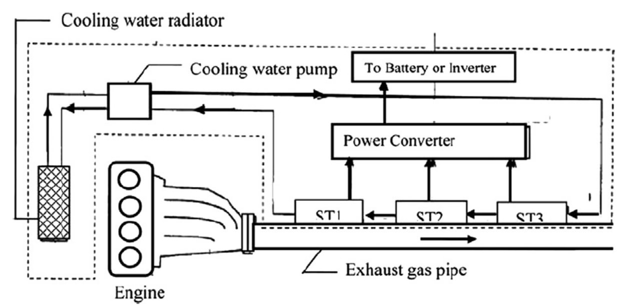



**Fig. 20.** Schematic diagram showing a recent patent applied to an automobile for converting waste heat directly into electrical power using a thermoelectric power generator [53].

thermoelectric generators. A bigger temperature difference could be achieved in this application due to the sufficient supply of cooling water in the circulation loop. However, extra energy needs to be consumed to maintain this cooling water circulation because of the presence of cooling water pump. Hence, this “enhancement” achieved by using water pump needs to be evaluated by considering the extra energy consumption of water pump when circulating liquid is used to extracting the heat at the cooling end.

Waste heat recovering at low temperature (250 °C) and medium temperature (550 °C) configurations have been discussed by BSST in partnership with BMW and Visteon, producing electric power from waste heat generated in the vehicle exhaust system and in the engine coolant loop.

With less than 25% of the energy content in the gasoline of most cars goes into useful work to move the vehicles, over 50% of the total fuel energy escapes to the ambient as heat loss primarily through the vehicle exhaust system and radiator. Different from other waste heat sources, waste heat from vehicular exhaust lies in a wide temperature range which extends from 100 °C to 800 °C. The temperature level depends on the driving conditions such as part load driving or full load driving. Therefore, developing vehicular thermoelectric generation system for recovering vehicle waste heat needs to take the following factors into account.

1. Varying thermal conditions caused by different driving conditions;
2. wide exhaust temperature range;
3. moving state.

Under general driving circumstances, the vehicle goes through different driving behaviors (such as acceleration, brake and stop) and varying road conditions (steep and bumpy) which make the engine and exhaust systems work in a varying condition to accommodate the changes. It can be referred in Fig. 21.

The driving load and fuel category decide the temperature level of exhaust gas. Different driving load requires vehicles to provide different amount of fuel energy to meet the varying driving needs. The driving load is proportional to the quantity of fuel consumption. The fuel type also determines the fuel consumption and the exhaust temperature. Currently, the commercial fuel type mainly includes gasoline and diesel. Fig. 22 shows the exhaust temperature across the exhaust and engine system of a typical car. The temperatures are shown in the comparisons of driving load (full load and part load) and fuel type (gasoline and diesel).

Waste heat is mostly generated in motion mode. The movement of vehicle necessitates the considerations of the impacts that the moving status imposes on TE modules enclosed in the thermoelectric generation system.

Considering the factors mentioned above, a successful design and construction of vehicular thermoelectric generation system must cover the following considerations:

1. Adopting temperature stabilizing method to eliminate excess temperature on the hot end of TE modules to avoid malfunctions (the welding points could be melted by excess temperature conditions caused by extreme driving conditions);
2. selecting the technically and economically suitable thermoelectric materials for waste heat recovery for the corresponding sections in the exhaust system is significant as the cost for fabricating the thermoelectric modules is proportional to the maximum operating temperature;

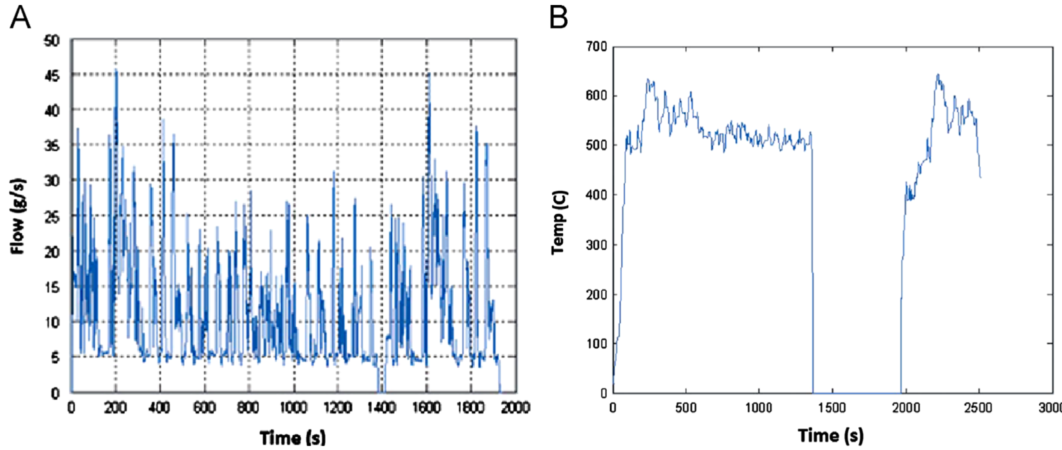
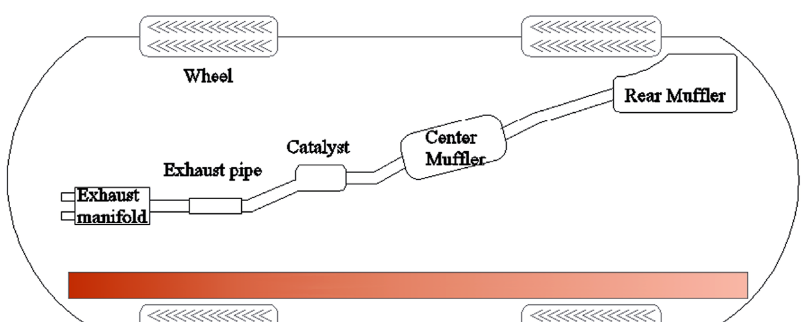



**Fig. 21.** Variation of automobile exhaust system, (a) mass flow rate; (b) temperature [70].




| | | | | | | |
|---|---|---|---|---|---|---|
| Gasoline | 790C | 620C | 560C | 480C | 430C | Full load |
| | 550C | 380C | 320C | 240C | 190C | Part load |
| Diesel | 600C | 430C | 370C | 290C | 240C | Full load |
| | 450C | 280C | 220C | 140C | 100C | Part load |

**Fig. 22.** Temperatures of exhaust system components for a gasoline engine and diesel engine [54].

3. accommodating the thermal and mechanical stresses under extreme driving conditions while maintaining an optimal thermal conductivity with TE modules as well as long cycle fatigue.

It was thought to be unattractive to employ thermoelectric power generation in automobile due to the high temperature thermal environment in automobile's exhaust/engine system. The high operating temperature requires high figure-of-merit material which turns out to be costly. However, considering the fact that both cars and trucks consume a considerable amount of fuel at low mass flow rates, especially when the vehicles are experiencing city driving where the fuel efficiency is much lower than that of highway driving due to the energy-inefficient operating such as varying speed, frequent braking and accelerating, improved fuel saving and reduced greenhouse gas emissions become the major impetuses for thermoelectric applications in vehicles. Thermoelectric power generation by recovering waste heat from automobile has become a highly necessary and promising approach. Many studies have reviewed its application in automobile engine/exhaust system and developed effective ways to recover the waste heat in automobile in an economical and optimum way. The possibility of recovering the waste heat with thermoelectric power generation was explored as early as 1914 [55, 56]. The waste heat recovery application on automobile has been investigated for over 90 years [57–60]. Some of them have developed thermoelectric generation systems which produce 0.5–1 kW electrical power with 5–10% overall efficiency [61, 62].

Thermoelectric applications on Porsche [63], truck [64] and passenger cars [65, 66], and military vehicle have been studied. The system shown in Fig. 23 is a joint effort of BMW, BSST and Visteon [67] which focused on waste heat recovery in exhaust gas and engine radiator in later phases and the fuel consumption was reduced by 8–12.5%. The system architecture adopted a primary heat exchanger that transfers waste heat in exhaust gas to thermoelectric generator via closed liquid loop. It claimed to have delivered higher efficiency compared to direct attachment to exhaust component due to improved thermal impedance match with exhaust gas, direct control of heat flux which facilitates electric load matching, thermodynamic cycle optimization and the heat transfer through a closed liquid. However, the system complexity needs to be considered in the evaluation of system reliability assessment.

A project with Hi-Z technologies was initiated by the U.S. Department of Energy in about 1995 to develop a thermoelectric generator to convert the waste heat from the engine of a heavy-duty class 7–8 diesel truck. This application using Bismuth Telluride material provided a nominal 1 kW. The TE unit was integrated with the muffle which is the component part with the lowest temperature level as shown in Fig. 24. So the using of bismuth telluride for recovering waste heat from this part is reasonable due to the matched operating temperature (up to 250 °C). Radiator cooling water (110 °C) was used to extract the heat from the cold side of TE unit.

For the application in automobile exhaust system, the effective application involves with a suitable design in terms of material

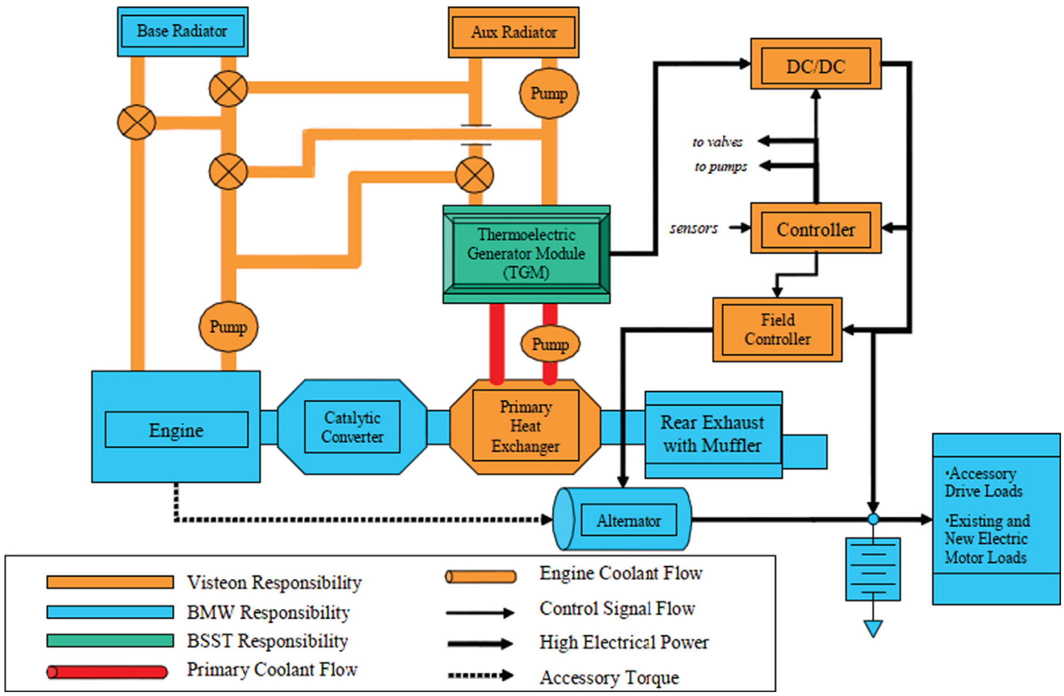



**Fig. 23.** Block diagram for waste heat recovery power generation system [67].

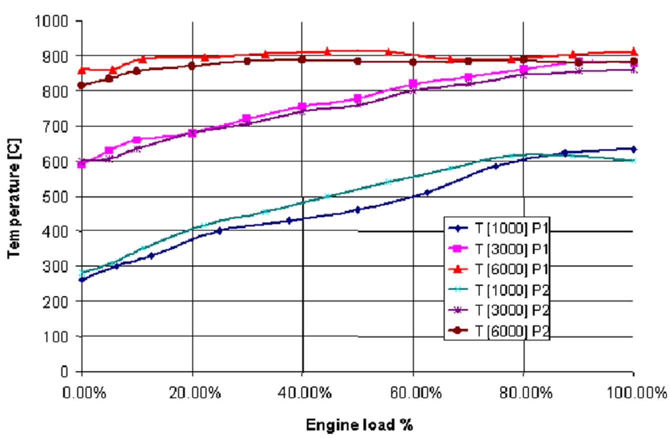



**Fig. 24.** Exhaust gas temperature s for different speeds (1000, 3000, 6000 RPM) measured in front of (P1) and behind (P2) the catalytic converter [68].

match and system architecture. PbTe was reported to be the most suitable for converting waste heat energy from automobiles into electrical power [69]. However, as mentioned previously, the temperature distribution lies in a very wide range which cannot be fully recovered by one type of material. A multistage heat recovery system with different materials optimally oriented for different temperature range shows more potential in effective recovery of total waste heat. Segmented materials which can recover waste heat efficiently from different temperature level are promising candidates of vehicular thermoelectric generators.

Conventional systems are designed to work optimally at a nominal operating condition, while maintaining the capability of operating at off nominal or extreme conditions without causing any system damage. In this situation, systems working in a narrow range of thermal power conditions are normally simplified due to the comparatively stable conditions. However, for the wide range, the overall average efficiencies are reduced by over 20% by designs compared to the achievable peak efficiency.

Automobile exhaust system gives out waste heat at varying rate due to the highly dynamic characteristic of automobile [70], especially typical passenger vehicles of which the engines run at an efficiency of about 25%. In most situations, a significant amount of waste heat is available to be recovered and converted to electricity. From the views of varying temperature and exhaust flow rate, a multi-section system with each section optimized for specific range of operating conditions has been constructed based on automobile exhaust system by Bell [71] to overcome the low efficiency caused by a broad range of thermal power input. Performance improvements of greater than 90% at low flow rates and of over 25% at high flow rates have been obtained for the proposed three section system over one section system. However, compared to one section system, due to the added valves, switches and pump, the proposed approach made the system more complex, higher-cost and less reliable. It would be more informative if a cost comparison and benefit output should was evaluated to judge the improved performance achieved by the modified design more comprehensively.

### 3.2.2. Aerospace

Explorations in hostile and inaccessible locations such as space, advances in medical physics, deployment of marine and terrestrial surveillance systems and earth resources require autonomous long-life sources of electrical power. Due to the characteristic of no moving parts, no position dependence and the good adaptability for various heat sources, thermoelectric generators have more than 100,000 h steady-state operation and precise temperature control [72]. Their developments first occurred in US space program, they have been used by NASA (National Aeronautics and Space Administration) to provide electrical power for spacecraft since 1961. Thermoelectric power generation system has a great application potential for a large number of different classes of space missions especially. As researches continue in power conversion field to improve configurations and specific designs, thermoelectric power generation keeps showing great strength for both short- and long-term space missions.

High performance radioisotope generators (RTG) are still of interest for deep space missions but the shift towards small, light space crafts has developed a need for advanced power sources. The development of thin film thermoelectric devices shows attractive potential. The development of light weight, high voltage devices with good performance is realizable with the employment of the combination of semiconductor technology, thermoelectric thin films and high thermal conductivity materials. The reliability of thermoelectric technology has been demonstrated in applications such as the Voyager spacecraft with Voyager 1 passing into the Heliosheath about 8.3 billion miles from Earth on May 24th 2006. The successful application also goes to TAGS-85 which has been used in numerous space and terrestrial applications [73]. These TAGS radioisotope thermoelectric generators (RTG) working over 20 years are still delivering enough power to support the Pioneer 11 (together with the pioneer 10, the pioneer 11 was the first to traverse the asteroid belt and visit the giant gas planets) spacecraft on board experiments and power the radio which is returning useful data back to earth. As far as is known, these are the longest lived autonomous electrical power sources ever produced. The same type of applications also provided long-lasting power to the Viking Landers 1 and 2 and other devices used in inaccessible or hostile areas like meteorological data collection and transmission system in off-coast areas and seismic detectors in Alaska.

For aircraft industry (both commercial and military), thermoelectric device can capture waste heat from the engine and operate over the entire aircraft flight envelope without affecting engine's performance, a temperature profile on a high by-pass engine can be seen in Fig. 25. Fuel consumption can be cut down and consequently the cost for passenger and cargo airlines could be reduced.

### 3.2.3. Industries

Industrial processes are usually procedures involving chemical or mechanical steps in the manufacture of an item or items on a very large scale. The process industries include food, beverages, chemicals, pharmaceuticals, petroleum, ceramics, base metals, coal, plastics, rubber, textiles, tobacco, wood and wood products, paper and paper products, etc. Industrial energy consumption accounted for more than a fifth of all UK energy consumption in 2001 consuming 35,152 thousand tonnes of oil equivalent and a steady rising trend is shown in Fig. 26 [75].

Due to the large scale in most cases, industries involve with a huge amount of energy consumption, in which a considerable amount escapes to ambient in the form of exhausting, radiation and cooling. Fig. 27 compares the energy use and losses in energy systems (steam systems, fired systems, and motor drive) across sixteen industrial sectors. Five industrial sectors which include petroleum refining, chemicals, forest products, iron and steel, and food and beverage, account for over 80% of all the energy inputs to energy systems. They are large users of steam systems and fired systems such as furnaces and dryers. In total, energy losses

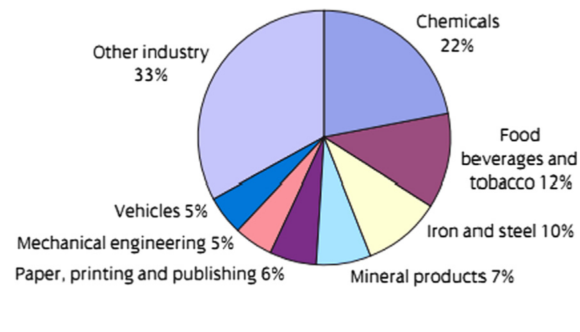



**Fig. 26.** Energy consumption distribution of industry sectors in the UK.

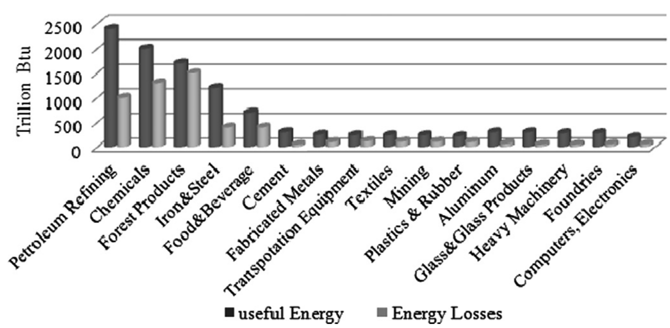



**Fig. 27.** Diagraph of energy consumption in different industrial sectors [76].

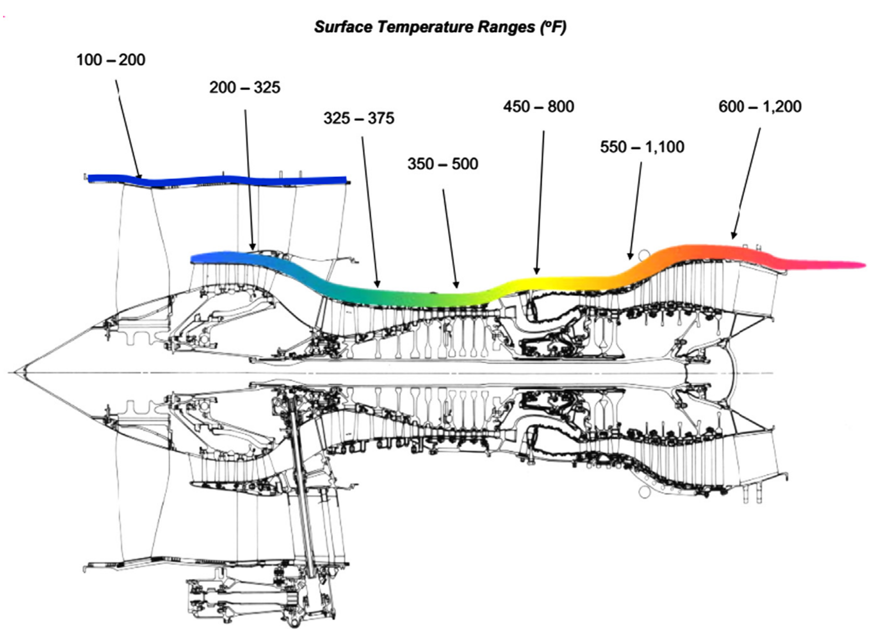



**Fig. 25.** Temperature profile of a high by-pass engine [74].

associated with energy systems in these five industries represents over 15% of the energy consumed by U.S. industry.

This unused energy is energy loss or waste heat, which is generated in the processes of fuel combustion and chemical reactions, then wasted by ending up in the environment rather the product due to unnecessary process, intensive drying, inefficient boilers and steam systems. Driven by the growing fuel prices and strong concerns on the global environment, industries find it necessary to develop and employ heat recovery approaches to cut down the energy consumption and consequently contribute to the reduction of greenhouse gas emission and environmental improvement.

Because of their high reliability, noiseless operation, low maintenance and long life, thermoelectric generation are preferred to other energy conversion devices particularly in harsh environments, despite of their relatively low efficiency. The type of thermoelectric material used for industrial utilities is dependent on the operating temperature range of the applied areas. For example, the available temperature ranges from 325 K to 1100 K for processing plants of combustible solid waste [77], depending on the used materials of the generators for different operating temperature ranges. In a typical steel plant, the furnace provides a steady source of convenient piped water which can be readily converted by thermoelectric generators into electricity when large amounts of cooling water were discharged at around 90 °C. Bismuth telluride thermoelectric material was employed to produce a total electrical power of 8 MW in major components of a modern steel plant [78].

The possibility of employing thermoelectric technology to generate electrical power from low temperature heat source on off-shore oil platforms was discussed in 1992 [79]. The oil reservoir located at a depth of around 3 km and the temperature at the working depth is in the range of 80–100 K. It was concluded that it was technically feasible to use thermoelectric power generation in this circumstance but the cost of transmitting dc power from the platforms to the adjacent mainland was considered to be uneconomic. If the electrical power can be stored by being converted to other type of energy like hydrogen, the high cost for the dc power transmission could have been avoided.

Applications in both small scale and large scale for recovering heat from combustible solid waste have been conducted [80, 81]. An estimated conversion efficiency of 4.36% was achieved in a small-scale on-site experiment using a 60 W thermoelectric module installed near the boiler section of an incinerator plant [82]. It was estimated that an output of 426 kW could be obtained according to an analysis of a conceptual large scale system burning 100 t of waste during a 16-h-working day. The possibility of utilizing the waste heat from incinerated municipal solid waste has also been considered and an on-site experiment using 60 W thermoelectric module was conducted. The module was installed near the boiler section of an incinerator plant where the waste gas temperature varied between 823 K and 973 K. An estimated conversion efficiency of about 4.4% has been achieved. Thermoelectric generators operating on natural gas, propane or diesel have been developed with different thermoelectric alloys with the maximum hot side temperature ranging from 525 K up to 875 K [83]. These devices have been used in various industrial applications for data acquisition and telecommunications.

### *3.2.4. Domestic application*

The domestic power generation using thermoelectric technology has been mentioned in previous studies. However, not many have looked into its application in building services. Unlike PV technology, thermoelectric technology does not rely on solar radiation only. It is useable on many types of heat sources, especially the rewarding waste heat from industrial sector, domestic sector and transportation sector.

Due to the energy conversion characteristic of thermoelectric technology, almost any heat resources existing in domestic environments are eligible for energy conversion. For example, the houses where wood/diesel/biomass burning stove or other available heating facilities are regularly used have a great potential to generate electrical power using thermoelectric generator. The first stove-top application [84] was developed by Royal Institute of Technology in Sweden in middle of 1990s. The application was integrated with domestic wood burning stove in remote area of northern Sweden where is far from the electricity grid. It would have cost too much to connect to the grid from the remote traditional farm houses in mountain areas. Generally, a gasoline powered motor electricity generator was used to provide the basic electricity for the need of lighting, TV, small appliances and other needs. It was too expensive to use it due to the high price of gasoline and too much maintenance is required. Moreover, it produces too much noise and the power output always exceeded the electricity requirements. Therefore, a thermoelectric generator showed its attractiveness and it was attempted to be installed onto the cooking stove in a house, shown in Fig. 28. The generator was comprised of two HZ-20 thermoelectric modules. The generator was installed at the left rear of the stove where the temperature was the highest and the family use was not interfered. A heat sink together with a 12 V (2.2 W) fan was used to keep the cold side temperature down by blowing low temperature air to the heat sink extrusions. The best performance was in the morning with a power output at 10 W when the ambient temperature was low and the stove was frequently fueled. During the day time, the power output ranged from 4–7 W. About 14 kg/cm$^2$ of pressure was loaded on the module by four sets of nuts and Bellville spring washers.

A similar application to home used stove has been studied and developed recently [85]. The energy efficiency of the stove could be improved by producing extra electrical power from the heat that is not used. However, both of them used a cooling fan to cool down the heat sink by blowing ambient air onto the heat sink extrusions. A few disadvantages caused by this include the moving

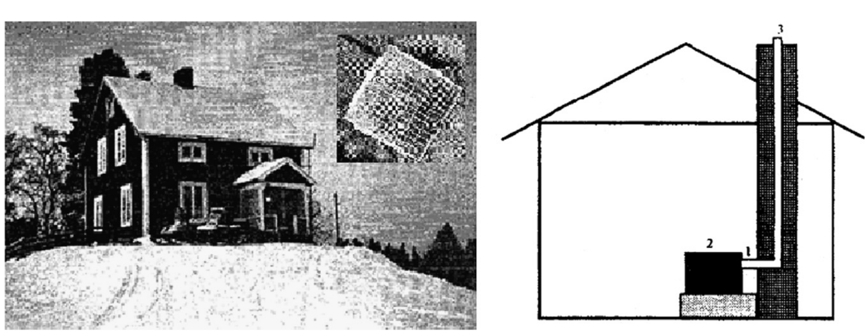



**Fig. 28.** The test site and installation diagram of the stove-top thermoelectric generator in Skerfa, Sweden [84].

parts of the cooling fan, the use of energy consuming fan and the unmanageable heat output.

Another example was given by its application in a domestic central heating system where the modules were located between the heat source and the water jacket [86]. It converts about 5% of heat output from the gas/oil burner into electrical power before the heat output reaches the central heating hot water exchanger and the remained 95% heat output is transferred to the hot water exchanger for space heating in the house. Therefore, recovering rejected heat for space heating and domestic hot water as part of a cogeneration thermoelectric system would make thermoelectric more attractive as overall thermal efficiency can be increased up to 80% [87, 88]. Gao [87] proposed a symbiotic application which uses the rejected thermal energy to improve the combustion process efficiency by pre-heating the air/fuel mixture to higher temperatures. Qiu [89] developed a thermoelectric power generation system which generates electricity and hot water by burning natural gas in a furnace. Relying on the supply of natural gas, its operation is suitable for the applications which are purposefully designed for using the natural gas as the primary fuel. Zheng [88, 90] proposed a cogeneration system which uses the heat from boiler exhaust and solar power in the UK residential houses. A potential benefit has been prospected for supplementing the domestic energy need and improving the energy efficiency in the UK domestic houses on the basis of available heat from boiler waste and solar energy.

#### 3.2.5. Thin film application

Thin films have attracted considerable attention because of their potential application in the micro-fabrication of integrated thermoelectric devices and its flexibility in installations. Due to the small thickness, thin film applications allow exceptionally high heat fluxes and low thermal resistances which deliver much higher power densities compared with conventional modules. Thin film thermoelectric device [91] is applied for power generation in high altitude, long duration communications platform where the heat was recovered from long wave infrared radiation leaving the surface of the earth. On the heat sink side, the heat is dissipated by radiation to the space. A temperature difference of 58 K was established in this design. A higher temperature difference, which is 85 K, has been achieved in [92] by adopting heat flow parallel to the film surface, different from conventional applications where the heat flow is vertical to the film surface.

However, the challenge of thin film applications lies in the growth process. Currently, there are quite a few advanced methods that have been developed to fabricate the thin film structure. Different from the commonly-used fabrication methods which include flash evaporation [93], hot wall epitaxy [94], sputtering [95], metal organic chemical-vapour deposition [96] and molecular beam epitaxy [97], co-evaporation [98] was claimed to require less preparation time, lower fabrication cost and be compatible with microelectronic processing. In the work, high-purity (99.999%) bismuth and telluride were evaporated from molybdenum boat and a tantalum crucible, respectively. The films were deposited by the co-evaporation of bismuth and telluride onto a heated, clean glass substrate. The best quality of thin films obtained using co-evaporation technology has $\alpha = 81\ \mu V/K$, $\rho = 0.32 \times 10^{-3}\ \Omega$ for p-type and $\alpha = -228\ \mu V/K$, $\rho = 1.30 \times 10^{-3}\ \Omega$ for n-type, respectively.

### 3.3. Summary

Table 2 summarizes the mainly experimental studies that have looked into thermoelectric applications of heat engine and power generation in vehicular, medical, electronic, aerospace, industrial and domestic areas. As a heat engine, the thermoelectric module can be used to provide effective cooling and heating in a wide range of areas at an adjustable rate. The ones listed in Table 2 are the ones that have been reported academically. However, it has also been or attempted to be used in other similar area such as portable mini fridge and radiant cooling wall panel either at commercial or research level. The material, operating temperature, power input (heat engine) and output (generation), conversion efficiency and thermal efficiency from the references have also been listed. Thin film application has been listed out separately due to its unique characteristics and advantages, which enable it to be used in a wider range of application areas. It has the potential of dominating the advanced thermoelectric application in the future to come.

## 4. Summary

The overall performance of thermoelectric system is determined by two major factors: the material properties and the system. Although this research is mainly focused on the system wise, the research work reviews the work on thermoelectric material, module construction and applications to show a full image of thermoelectric research and the applications.

In order to make the thermoelectric application more economically feasible, increasing efforts have been made to discover and develop advanced thermoelectric materials with high figure-of-merit. Fabrication methods such as super-lattice, plasma treatment, segmented element, nano-composite and nanostructure to improve ZT value of thermoelectric materials have been introduced.

**Table 2**
Thermoelectric applications in different areas.

| Application | Area | References | Material (s) | Purpose (s) | Operating temperature (cold/hot) | Power input (output) | Conversion efficiency | Thermal efficiency |
|---|---|---|---|---|---|---|---|---|
| Heat engine | Vehicle | [45] | BiTe based | Cooling and heating | Not specified | n/a | n/a | Not specified |
| | Medical service | [46] | Not specified | Cooling | 283 K/318 K | 12 V/4 A | n/a | Not specified |
| | Electronic | [47–51] | CdZnTe | Cooling | 283 K/313 K | 3 W | n/a | Not specified |
| Power generations | Automobile | [61,62] | $Bi_2Te_3$, PbTe | Electricity generation | 373 K/1073 K | 0.5–1 kW | 5–10% | n/a |
| | Aerospace | [73] | PbTe, SiGe | Electricity generation | 366 K/783 K–1300 K | 25–56 W | Not specified | n/a |
| | Industrial | [80–82] | SiGe | Electricity generation | 293 K/871 K | 46.8 W | 4.4% | n/a |
| | Domestic | [84,87–89] | $Bi_2Te_3$, PbTe | Electricity and hot water generation | 303 K/473 K–911 K | 4 W–1 kW | 4.0% | 60%–80% |
| | Thin film | [92] | ZnSb, $Bi_2Te_3$ | Electricity generation | Not specified ($\Delta T = 85$ K) | 19.13 μW | Not specified | n/a |

*Note*: "Not specified" means the result is not mentioned in the reference; "n/a" means the result is not applicable to the parameter.

These methods have shown positive results by changing the material properties and improving module shape and structure, such as reducing thermal conductivity, enhancing electrical conductivity and adopting novel module shape and structure, such as ring-shape and thin film.

With continuous efforts, the difficulty in making a breakthrough in material research and development in terms of fabrication, construction and commercialization is still one of the major factors that have limited thermoelectric application to only specialised areas. However, due to the advantages of no moving parts, long lifespan and quiet operation, thermoelectric modules, in attempts, have been used in many areas such as automobile, aerospace, industries and domestic sector. They have not been used as widely and intensively as expected due to lack of economical feasibility. The energy efficiency of conventional thermoelectric applications is far too less to compensate the system cost due to low conversion efficiency, and only suitable for micro/small applications or some specialised areas. Nevertheless, the immense potential and prospect are enlightened by the results shown in the research conducted in laboratories environments. It would become a more significant green energy solution when the research efforts, either on advanced materials or economically feasible applications, walk out from the research environment into the commercial stage.

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